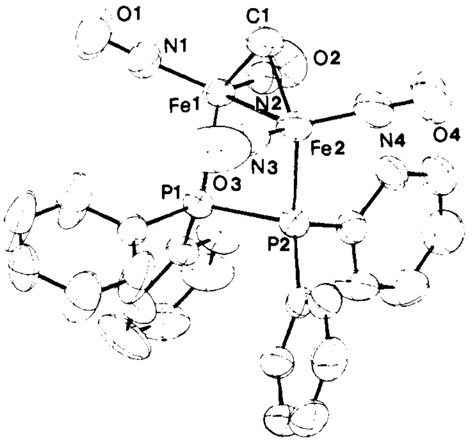

Figure 2. ORTEP drawing of **6**.

ically,[6] can also be obtained by reduction of **1** with $LiAlH_4$ or $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ in THF. By way of contrast, treatment of **1** with 1 equiv of $LiBEt_3H$ in THF at ca. −24 °C results in the formation of a red-brown solution of Li^+**3**. The air-sensitive but thermally stable (at ambient temperatures) monoanion **3**[7] contains a bridging NO, a bridging PPh_2 supported by an Fe–Fe bond,[1a] and a terminal PPh_2H, with the PH hydrogen originating from the reducing agent (**1** and $LiBEt_3D$ yield Li^+**3**-d_1).

When a THF solution of Li^+**3** was treated with 1 equiv of *n*-BuLi at −78 °C, immediate reaction occurred as evidenced by color change to bright red. The deprotonated binuclear species is provisionally assigned structure **4**.[8] It is thermally unstable and at ca. −70 °C in solution readily isomerizes to **2**.

Solutions of $(Li^+)_2$**4** and Li^+**3** represent convenient entries to the novel isomeric complexes **5** and **6**. Thus, the former rapidly reacts with CH_2I_2 at −78 °C to yield **5**, which was isolated (ca. 20%) at 25 °C as a red, air-stable solid.[9] Reaction of Li^+**3** with CH_2I_2 commences at ca. −63 °C to afford **6**, which was isolated (35%) at 25 °C, along with **5** (<5%), as a deep red, moderately air-stable solid. Both **5** and **6** were characterized by X-ray crystallography, and their molecular structures are shown in Figures 1 and 2, respectively. Since **5** was not detected when the latter reaction was monitored by ^{31}P NMR spectroscopy, its formation must have occurred during workup. Indeed, **6** undergoes unprecedented isomerization to **5** on heating in THF solution. This conversion is complete within 20 h at 55 °C, with **1** also being produced.

Whereas the formation of **5** from **4** and CH_2I_2 is not unexpected, that of **6** from **3** and CH_2I_2 invites comment. The former likely proceeds by interaction of the CH_2I_2 or CH_2I_2-derived carbon with the terminal PPh_2 group, followed by rapid completion of the μ-CH_2PPh_2 bridge. Since the first step of such a sequence is blocked for the reaction of CH_2I_2 with **3**, initial interaction of the carbon probably occurs with $Fe_{(1)}$. The formation of $Fe_{(1)}(\mu\text{-}CH_2)Fe_{(2)}$ may then continue by dissociation of PPh_2H and oxidative addition of $Fe_{(1)}CH_2I$ to $Fe_{(2)}$. Several pathways to the $Fe_{(1)}(\mu\text{-}Ph_2PPPh_2)Fe_{(2)}$ bridge in **6** may be proposed; the formation of μ-Ph_2PPPh_2 is unusual since reactions of P_2R_4 with metal carbonyls and nitrosyls commonly afford phosphido-bridged binuclear complexes.[10]

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (through Grant CHE-7911882), Ministero Pubblica Istruzione (Rome), and NATO (through Grant 068.81).

Registry No. 1, 14917-04-5; $(Na^+)_2$**2**, 89958-70-3; Li^+**3**, 89958-71-4; $(Li^+)_2$**4**, 89958-72-5; **5**, 89958-73-6; **6**, 89958-74-7.

Supplementary Material Available: Crystal data, final positional and thermal parameters, selected bond lengths and bond angles, and spectroscopic data for **5** and **6** (9 pages). Ordering information is given on any current masthead page.

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[6] Dessy, R. E.; Kornmann, R.; Smith, C.; Haytor, R. *J. Am. Chem. Soc.* **1968**, *90*, 2001. No spectroscopic data were reported for **2**, however.

[7] Li^+**3**: IR (THF) $\nu_{N\equiv O}$ 1704 m, 1660 s, $\nu_{N=O}$ 1420 w–m cm^{-1}; $^{31}P\{^1H\}$ NMR (THF, 25 °C) δ 164.6 (d), 43.4 (d, J_{PP} = 19.6 Hz), temperature invarient to −73 °C; ^{31}P NMR (THF, 25 °C) δ 164.6 (s, br), 43.4 (d, br, $^1J_{PH}$ = 338 Hz). Li^+**3**-d_1: $^{31}P\{^1H\}$ NMR (THF, 25 °C) δ 164.0 (d), 42.2 (dt, J_{PP} = 20, $^1J_{PD}$ = 50 Hz). Na^+**3** and K^+**3** (from **1** and appropriate $MBEt_3H$): IR (THF) $\nu_{N=O}$ 1435 w–m cm^{-1}.

[8] $(Li^+)_2$**4**: $^{31}P\{^1H\}$ NMR (THF, −78 °C) δ 159.6 (d), 20.5 (d, J_{PP} = 50 Hz); similar ^{31}P NMR (THF, −78 °C), i.e., no one-bond P–H coupling for signal at δ 20.5.

[9] In contrast, $(Li^+)_2$**2** and CH_2I_2 at −78 °C followed by warming to 25 °C afford 80–90% **1**, but no detectable **5**.

[10] (a) Hieber, W.; Kummer, R. *Z. Anorg. Allg. Chem.* **1966**, *344*, 292. (b) Hayter, R. G.; Williams, L. F. *Inorg. Chem.* **1964**, *3*, 717.

Synthesis of 1-Azaazulene and Benz[*a*]azulene by Carbene Rearrangement

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The ring expansion of arylcarbenes to cycloheptatrienylidenes/cycloheptatetraenes has been the subject of numerous mechanistic investigations,[1] but this reaction has found little use in the synthesis of seven-membered ring compounds. In fact, the equilibrating tolylcarbenes are trapped by methyl groups in the form of benzocyclobutene and styrene,[1,2] but no corresponding intramolecular trapping products of the methylcycloheptatrienylidenes/methylcycloheptatetraenes have been reported. We now find that it is indeed possible to trap these seven-membered ring intermediates and to put the reaction to synthetic use in the preparation of azulene derivatives.

The initial experiments were not very encouraging: flash vacuum pyrolysis of the sodium salt of fluorene-2-carboxaldehyde tosylhydrazone[3] at 400 °C (10^{-3} torr) gave a 1.5% yield of benz[*a*]azulene (**8**) together with a 2.0% yield of 4,8-dihydrocyclopenta[*d.e.f*]fluorene (**9**).[4]

Much better results were obtained with a different carbene precursor, 5-(2-fluorenyl)tetrazole (**2**), obtained by addition of HN_3 to the nitrile **1**.[5] The pyrolysis of **2** (1 g) at 420 °C (10^{-1}–10^{-3} torr) gave a 44% yield of benz[*a*]azulene (**8**) together with 4% of **9** (Scheme I). As is typical of tetrazoles, a cycloreversion to 2-cyanofluorene (**1**), isolated in 33% yield, also occurred. The products were separated by preparative gas chromatography (SE 30, 135 °C) and identified by spectral comparison with authentic samples.[6,7]

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[1] Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173. Jones, W. M.; Brinker, U. H. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; p 109. Wentrup, C. "Reactive Molecules"; Wiley: New York, 1984.

[2] Baron, W. J.; Jones, M., Jr.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 4739.

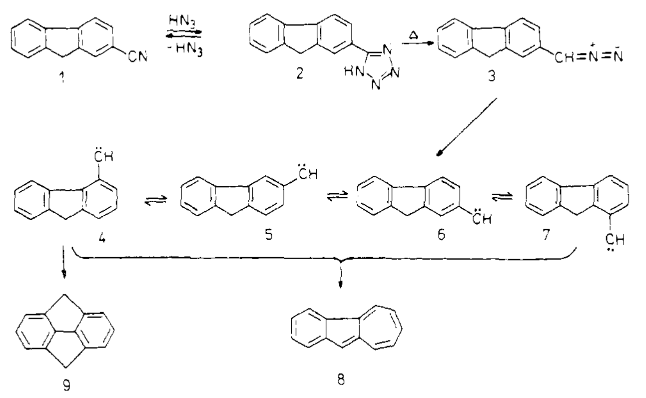
[3] Fluorene-2-carboxaldehyde tosylhydrazone: mp 190–192 °C; correct elemental analysis (C, H, N) was obtained. The sodium salt was prepared with NaH in ethanol–ether 1:1 (25 °C, 1 h), filtered under N_2, and dried at 50 °C (10^{-2} torr) for 8 h.

[4] Alder (Alder, R. W. University of Bristol, UK, private communication) has independently observed the formation in low yield of benz[*a*]azulene on pyrolysis of the sodium salt of fluorene-2-carboxaldehyde tosylhydrazone. The presence of **9** was assumed but not ascertained.

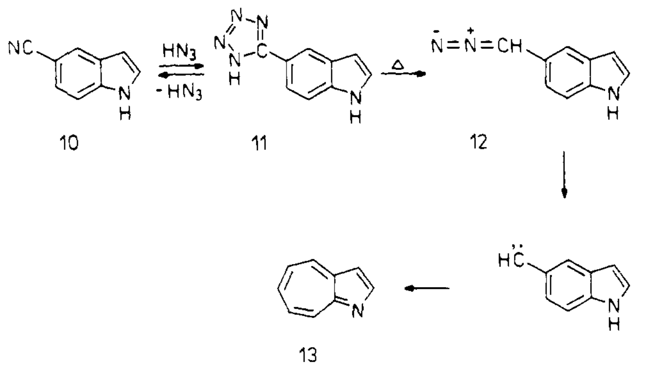
[5] **2** was obtained in 67% yield from **1** with NaN_3/NH_4Cl in DMF at 120 °C for 12 days: mp (dec) 252 °C; ^1H NMR (Me_2SO-d_6, 400 MHz) δ 8.26 (s, 1 H), 8.13 (d, 1 H), 8.08 (d, 1 H), 8.00 (d, 1 H), 7.64 (d, 1 H), 7.45 (t, 1 H), 7.39 (t, 1 H), 4.05 (s, 2 H), 3.5 (br, 1 H); mass spectrum *m/z* 234.0891 (calcd for $C_{14}H_{10}N_4$, 234.0905); correct elemental analysis (C, H, N) was obtained.

[6] Benz[*a*]azulene: ^1H NMR ($CDCl_3$, 400 MHz, integral 1 H in each instance) δ 8.40 (d, J = 8 Hz), 8.32 (d, J = 8.3 Hz), 7.97 (d, J = 10.9 Hz), 7.89 (t of d, J = 1 and 8 Hz), 7.70 (ddd, J = 1, 7, and 8 Hz), 7.50 (ddd, J = 1, 7, and 8 Hz), 7.35 (s), 7.21 (tdd, $J \leq 0.7$, 8.3, and 10.6 Hz), 7.05 (tdd, $J \leq 0.7$, 8.3, an 10.6 Hz), 6.86 (ddd, $J \leq 0.7$, 8.3, and 10.9 Hz); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 142.5, 140.6, 139.2, 135.9, 134.6, 131.9, 128.5, 127.9, 125.4, 123.7, 121.8, 120.8, 120.3, 116.1. This compound was identified by comparison with a sample prepared according to Alder and Whittaker.[8]

Scheme I



Scheme II



Evidence for the intermittant formation of 2-(diazomethyl)-fluorene (**3**) was obtained by pyrolyzing **2** at 380 °C (10^{-4} torr) and condensing the product on a −196 °C KBr disk, thereby allowing the observation of a strong IR absorption at 2060 cm^{-1}. The formation of the products **8** and **9** is rationalized in terms of the equilibrating arylcarbenes **4–7**. Carbene **4** undergoes insertion into the peri C–H bond to give **9**. Ring expansion[1] of the carbenes **4–7** followed by a hydrogen shift gives **8**.

The preparative advantage of this synthesis of benz[*a*]azulene is readily seen when comparing with the 0.5% yield of the best current preparation from fluorene and ethyl diazoacetate.[8]

The usefulness of the tetrazole pyrolysis is further seen in our preparation of 1-azaazulene (**13**), an otherwise difficultly accessible and unstable compound previously prepared in a lengthy synthesis in low yield.[9] 5-Cyanoindole (**10**) was converted to the tetrazole **11** with HN_3.[10] Pyrolysis of **11** at 350 °C (10^{-4} torr) allowed the detection of 5-diazomethylindole (**12**; 2060 cm^{-1}). At 500 °C (10^{-1}–10^{-3} torr) 1-azaazulene[11] (**13**) was formed in 50% yield together with 30% of the product of cycloreversion, viz., 5-cyanoindole (**10**) (Scheme II). Thus, 1-azaazulene is readily available in a two-step synthesis from commercial **10**.

If the nascent carbene function is moved from the six-membered to the five-membered ring in compounds of the types **3** and **12**, the corresponding benzenoid hydrocarbons are formed in place of azulenes. Thus, we prepared the sodium salts of the tosylhydrazones of indene-2-carboxaldehyde, indole-3-carboxaldehyde, and fluorene-9-carboxaldehyde, which, on pyrolysis at 650 °C (10^{-3} torr) gave naphthalene, quinoline, and phenanthrene in isolated yields of 66%, 30%, and 50%, respectively.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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(7) 4,8-Dihydrocyclopenta[*d.e.f*]fluorene: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.34 (d, J = 7 Hz, 2 H), 7.16 (t, J = 7 Hz, 4 H), 4.31 (s, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.3 (s), 127.8 (d, J = 158 Hz), 126.5 (s), 124.4 (d, J = 158 Hz), 44.1 (t, J = 133 Hz). This compound was identified by comparison with a sample prepared according to: Trost, B. M.; Kinson, P. L. *J. Am. Chem. Soc.* **1970**, *92*, 2591.

(8) Alder, R. W.; Whittaker, G. *J. Chem. Soc., Perkin Trans 2* **1975**, 714.

(9) Nozoe, T.; Seto, S.; Matsumura, S.; Terasawa, T. *Chem. Ind.* (*London*) **1954**, *30*, 1356, 1357. Nishiwaki, T.; Abe, N. *Heterocycles* **1981**, *15*, 547.

(10) **11**: mp 245 °C dec; ^1H NMR (Me_2SO-d_6, 400 MHz) δ 11.50 (s, 1 H), 8.31 (s, 1 H), 7.81 (d, 1 H), 7.60 (d, 1 H), 7.48 (s, 1 H), 6.59 (s, 1 H), 6.5 (br, 1 H); mass spectrum, *m/z* 185.0773 (calcd for $C_9H_7N_5$, 185.0782); correct elemental analysis (C, H, N) was obtained.

(11) **13**: picrate mp 196–197 °C dec (lit.[9] 197–198 °C); UV (CH_3OH) λ 340, 330, 310, 260, 230 nm; ^1H NMR (CD_3OD, 400 MHz) δ 9.26 (d, J = 10 Hz, 1 H), 9.14 (d, J = 10 Hz, 1 H), 8.09 (d, J = 3 Hz, 1 H), 8.66 (t, J = 10 Hz, 1 H), 8.49 (t, J = 10 Hz, 1 H), 8.43 (t, J = 10 Hz, 1 H), 7.69 (d, J = 3 Hz, 1 H); mass spectrum, *m/z* 129 (M^+).

Additions and Corrections

Template Effects. 6. The Effect of Alkali Metal Ions on the Formation of Benzo-3*x*-crown-*x* Ethers over a Wide Range of Ring Sizes [*J. Am. Chem. Soc.* **1984**, *106*, 168]. LUIGI MANDOLINI* and BERNARDO MASCI*

Page 171: The corrected form of eq 3 is

$$k_{\mathrm{obsd}} = \frac{k_i + k_{ip}K_{\mathrm{ArO}^-}\gamma_{\pm}^2[\mathrm{M}^+] + k_{it}K_{\mathrm{ArO}^-}K_{\mathrm{ArO}^-\mathrm{M}^+}\gamma_{\pm}^2[\mathrm{M}^+]^2}{1 + K_{\mathrm{ArO}^-}\gamma_{\pm}^2[\mathrm{M}^+] + K_{\mathrm{ArO}^-}K_{\mathrm{ArO}^-\mathrm{M}^+}\gamma_{\pm}^2[\mathrm{M}^+]^2} \quad (3)$$